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Vibrational spectra of 2-phenyl-4H-3, 1- benzoxazin-4-one studied by IR spectroscopy and AM1 semiempirical molecular orbital calculations

V B Singh*, Amareshwar Kumar Rai, S K Mishra and V K Pandey

Department of Physics, Udai Pratap Autonomous College, Varanasi-221 002, Uttar Pradesh, India

E-mail : vipin_vns@sify.co

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Abstract : FTIR and Raman spectra of a leading bleach activator 2-phenyl-4H-3,1-benzoxazin-4-one have been recorded in the region 200–4000 cm^{-1} and 400–3200 cm^{-1} respectively. Vibrational frequencies for the fundamental modes of this polycyclic heteroatomic molecule have been calculated using Austin method1 (AM1) semiempirical molecular orbital method. Vibrational assignments have been made for the fundamental modes and the observed combination and overtone bands are also assigned. The carbonyl frequency (C=O) is observed at ~1766 cm^{-1} whereas the C=N stretching vibration is observed at 1611 cm^{-1} in the FTIR spectrum. The net atomic charges for each atom as well as the heat of formation of this molecule are also calculated

Keywords : Vibrational spectra, 2-phenyl-4H-3,1-benzoxazin-4-one, FTIR and Raman spectra, semiempirical (AM1) molecular orbital calculations.

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1. Introduction

2-Phenyl1-4H-3,1-benzoxazin-4-one (Figure1) also known as benzoylenthranil, is a leading bleach activator and belongs to an interesting class of tricyclic heteroatomic molecule. It is cost effective, environment-friendly and provides effective bleaching at as low as 40°C [1]. It is readily synthesized by different methods and there is enormous scope for obtaining diverse other compounds using this molecular species, as they undergo a variety of reactions [2–7]. Due to these properties, this molecule has been the subject of research by synthetic chemists for a long time; however, studies on the spectroscopic properties for this species are still lacking [3,4].

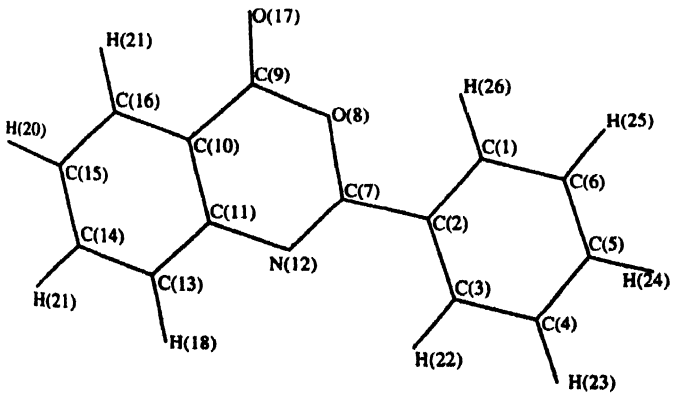

Figure 1. Structure of 2-phenyl-4H-3,1-benzoxazin-4-one after AM1 optimization.

Many researchers [8–12] are interested in determining an accurate vibrational potential field and frequency assignment for the polycyclic heteroatomic molecules. Attempts are continuously being made to determine accurate potentials and make reliable vibrational assignments for such molecules [8–12].

In the present work, we have recorded the Raman and IR spectra of 2-phenyl1-4H-3,1-benzoxazin-4-one. The AM1 (Austin Model 1) semiempirical molecular orbital calculations were performed to estimate the fundamental vibrational frequencies, net atomic charges as well as heat of formation of this molecule. Each calculated vibrational mode was visualized using the MOLDEN computer software in order to assist in their assignments.

*Corresponding Author

2. Experimental

The sample of 2-phenyl1-4H-3,1-benzoxazin-4-one in the powder form was synthesized in the Department of Applied Chemistry, I.T., B.H.U. using the method given by Errede [3]. FTIR spectra of this sample was recorded in the form of a nujol mull on a Jasco FTIR spectrometer model 5300 in the region 400–4000 cm^{-1} at a resolution of 4 cm^{-1}. The IR spectrum of this molecule was also recorded in the form of a KBr pellet on a Perkin-Elmer model-883 IR spectrometer at a resolution of 2.4 cm^{-1} in the region 200 –4000 cm^{-1}. The two IR spectra are consistent with each other. Raman spectra of this sample in the form of a pellet has been recorded on a Spex spectrometer model 1877-E in the spectral region 400–3200 cm^{-1}. A 5W Ar-ion laser at 514.5 nm with an out put on about 300 mw was used as the exciting source.

3. Computational method

The normal mode frequencies for this molecule have been calculated using MOPAC 5.1 computer program, which is based on the NDDO approximation at the AM1 level [13]. In this computer program, the total energy of the system is calculated. The first derivative of the energy is then obtained analytically while the second derivatives are evaluated by the finite difference method. The matrix of the second derivatives is suitably weighted and used along with the GF formalism [14] to obtain the frequencies and normal modes.

Band assignment has been made on the basis of which atom pair contributes maximum energy to specific mode. The mode of vibration is also confirmed through visual observation of all the molecular vibration through MOLDEN software.

4. Results and discussion

The 2-phenyl1-4H-3,1-benzoxazin-4-one molecule has C_s symmetry and hence all its 72 vibrational modes are infrared active. The normal modes are distributed as 49*A*' (symmetric) and 23*A*" (antisymmetric). The symmetry and antisymmetry are with respect to symmetry plane which is the plane of molecule itself.

We have observed more than 25 bands in the infrared spectrum of this molecule; however, only a few weak bands were observed in the Raman spectrum. The calculated vibrational frequencies were compared against the experimental data. Due to the neglect of anharmonicity and electron correlation, there is a systemic error between calculated and experimental vibrational frequencies. The calculated frequencies will be higher than the expected values. Therefore, we have corrected the calculated values of the vibrational frequencies with an average scaling factor of 0.92 as used in our earlier work [10–12]. However, a better correlation could be obtained by using specific scaling factors for stretching, in-plane bending and out of plane bending vibrations [8,9,15]. For fixing up the mode assignment, well-established spectral range of the characteristic group frequencies was also kept in mind. Experimental and calculated wave numbers for all the 72 fundamental modes of vibration with their corresponding assignment are given in Table 1.

Table 1. Vibrational assignments, experimental and calculated wave numbers (with relative intensities) of 2-phenyl-4H-3,1-benzoxazine-4-one

Vibrational number	Symmetry	Approximate description of vibration	Calculated (unscaled) (cm^{-1})	Calculated (scaled) (cm^{-1})	IR (Nujol mull) (cm^{-1})	IR (KBr pellet) (cm^{-1})	Raman (cm^{-1})
1	*A*"	Skeleton def.	12.27	11.28	-	-	-
2	*A*"	Skeleton def.	53.58	49.29	-	-	-
3	*A*"	Skeleton def.	107.30	98.72	-	-	-
4	*A*"	Ring torsion	115.22	106.00	-	-	-
5	*A*'	C-C-C bending	144.69	133.11	-		-
6	*A*'	Skeleton def.	176.83	162.68	-	-	-
7	*A*"	Skeleton def.	278.21	255.95	-	200 (S)	-
8	*A*'	C-C-C bending	292.66	269.25	-	-	-
9	*A*'	C-C-C bending	326.36	300.25	-	244 (M)	-
10	*A*"	Ring def.	368.08	338.63	-	-	-
11	*A*'	C-C-C bending	375.80	345.74	-	285 (W)	-
12	*A*"	Ring breathing	410.56	377.72	-	-	-
13	*A*"	Ring breathing	442.95	407.51	-	-	-

Table 1. *(cont'd)*

Vibrational number	Symmetry	Approximate description of vibration	Calculated (unscaled) (cm^{-1})	Calculated (scaled) (cm^{-1})	IR (Nujol mull) (cm^{-1})	IR (KBr pellet) (cm^{-1})	Raman (cm^{-1})
14	A''	C-N-C bending	515.53	474.29	-	-	-
15	A'	C-C-C bending	543.66	500.17	-	-	-
16	A'	O=C-O bending	566.11	520.82	442 (M)	450 (W)	-
17	A''	N=C-O bending	610.80	561.94	-	-	-
18	A'	C-N=C bending	625.70	575.64	-	-	-
19	A'	Ring Folding	645.62	593.97	530 (M)	523 (M)	-
20	A''	O=C-C bending	657.66	605.05	530 (M)	523 (M)	-
21	A'	C-C-C bending	659.41	606.66	-	-	-
22	A'	Skeleton def.	718.10	660.65	582 (W)	587 (VW)	-
23	A''	C-C-C bending	748.77	668.87	626 (M)	625 (M)	-
24	A''	C-C-C bending	796.68	732.95	-	-	-
25	A''	CH-wagging in phenyl	820.90	755.23	-	-	-
26	A''	CH-wagging in benzene	825.40	759.37	684 (S)	684 (VS)	-
27	A'	C-C-C bending	869.95	800.35	-	-	-
28	A''	CH-wagging in phenyl	891.43	820.12	-	-	-
29	A''	CH-wagging in benzene	930.10	855.69	765 (S)	764 (S)	-
30	A'	C-C-C bending	958.05	881.41	-	-	-
31	A''	CH-wagging in phenyl	967.37	889.98	-	-	-
32	A''	CH-wagging in benzene	983.88	905.17	-	-	-
33	A'	C-C-C bending	991.93	912.58	-	-	-
34	A''	CH-wagging in phenyl	993.49	914.01	-	-	-
35	A''	CH-wagging in benzene	1009.27	928.53	-	-	-
36	A''	CH-wagging in phenyl	1011.72	930.78	-	-	-
37	A''	Ring def.	1105.86	1017.39	922 (VM)	915 (VW)	-
38	A'	Ring def. in benzene	1167.22	1073.84	980 (VW)	-	-
39	A'	CH-bending	1184.92	1090.13	-	-	-
40	A'	Ring def. in phenyl	1188.48	1093.40	-	-	-
41	A'	CH-bending	1192.79	1097.37	1000 (W)	1000 (W)	1003(W)
42	A'	CH-bending	1198.48	1102.60	-	-	-
43	A'	CH-bending	1204.36	1108.01	1010 (M)	1010 (S)	1011(W)
44	A'	CH-bending	1253.72	1153.42	1060 (M)	1053 (S)	1060(W)
45	A'	C-O stretching	1278.01	1175.77	-	-	-
46	A'	CH-bending	1300.24	1196.22	-	-	-
47	A'	C-O str.	1300.24	1196.22	-	-	-
48	A'	CH-bending	1311.43	1206.52	1110 (W)	1112 (M)	-
49	A'	C-C stretching	1367.06	1257.70	1180 (W)	1180 (W)	-
50	A'	C-C stretch	1388.51	1277.43	1220 (W)	1222 (W)	-
51	A'	C-C and C-O mixed stretch vibration	1432.81	1318.19	1257 (S)	1252 (S)	1259 (S)
52	A'	C-C and C-O mixed stretch vibration	1467.23	1340.85	-	-	-
53	A'	C-C stretching	1480.23	1361.81	1313 (S)	1313 (S)	-
54	A'	Ring vib. phe. ring	1570.50	1440.86	1377 (M)	1380 (VM)	-
55	A'	C-C stretching	1601.83	1473.68	-	-	-
56	A'	C-C stretching	1624.63	1494.66	-	-	-
57	A'	C-N stretch	1657.24	1524.66	1464 (VS)	1466 (S)	-
58	A'	C=C stretching	1742.05	1602.69	1534 (W)	-	-
59	A'	C=C stretching	1763.60	1622.51	1553 (VW)	-	-

Table 1. *(cont'd)*

Vibrational number	Symmetry	Approximate description of vibration	Calculated (unscaled) (cm^{-1})	Calculated (scaled) (cm^{-1})	IR (Nujol Mull) (cm^{-1})	IR (KBr pellet) (cm^{-1})	Raman (cm^{-1})
60	A'	C=C stretching	1770.56	1628.91	-	-	-
61	A'	C=C stretching	1779.43	1637.08	1567 (M)	1567 (M)	-
62	A'	C=N stretching	1854.75	1706.37	1614 (S)	1611 (S)	1621(M)
63	A'	C=O stretching	2089.41	1922.26	1763 (VS)	1766 (VS)	1745 (W)
64	A'	CH-stretching	3168.91	2915.40	-	-	-
65	A'	CH-stretching	3172.81	2918.92	-	-	-
66	A'	CH-stretching	3175.46	2921.42	-	-	-
67	A'	CH-stretching	3175.76	2921.70	-	-	-
68	A'	CH-stretching	3182.69	2928.07	-	-	-
69	A'	CH-stretching	3186.39	2931.48	-	-	-
70	A'	CH-stretching	3189.09	2933.96	-	-	-
71	A'	CH-stretching	3194.66	2939.08	-	3041 (M)	-
72	A'	CH-stretching	3197.75	2941.93	-	3041 (M)	-

Table 2. Calculated values of net atomic charges of 2-phenyl-4H-3,1-benzoxazin-4-one after AM1 optimization.

Atom no.	Type	Net atomic charges
1	C	-0.1891
2	C	0.0513
3	C	-0.1185
4	C	-0.0883
5	C	-0.1504
6	C	-0.0512
7	H	0.1562
8	H	0.1407
9	H	0.1430
10	H	0.1580
11	C	0.3523
12	O	-0.2357
13	C	0.1991
14	N	-0.2071
15	C	-0.0665
16	O	-0.2859
17	C	-0.0730
18	C	-0.1482
19	C	-0.0987
20	C	-0.1448
21	C	-0.0773
22	H	0.1573
23	H	0.1388
24	H	0.1364
25	H	0.1404
26	H	0.1612

A very strong absorption peak observed in the IR of this molecule at ~1766 cm^{-1} is ascribed to carbonyl (C=O) stretching vibration whereas a strong peak observed at ~1611 cm^{-1} is ascribed to C=N stretching vibration. C=C stretching vibrations are observed in both the IR and Raman spectra of this molecule.

A broad IR band observed near 3041 cm^{-1} is ascribed to CH-stretching vibration. A number of combination and overtone bands are also observed in IR spectrum. The combination bands due to ($\nu_1 + \nu_{26}$), ($\nu + \nu_{62}$), ($\nu + \nu_{63}$) and ($\nu_{57} + \nu_{62}$) are readily identified in the IR at 882, 1850, 1966 and 3077 respectively and an overtone $2\nu_{20}$ is observed at 1040 cm^{-1}.

The values of the net atomic charges for each atom in 2-phenyl1-4H-3,1-benzoxazin-4-one are presented in Table 2. The calculated value of heat of formation and total energy of this molecule is 4.82712 kcal and -2762.53048 eV respectively.

5. Conclusion

The vibrational assignments of this bleach activator have been performed with the help of IR spectra and semiempirical molecular orbital calculations. These investigations will be helpful, to identify ground state vibrations of the above polycyclic heteroatomic molecule as well as in the identification of the modes of vibrations of other similar molecules. The excited states vibrations can also be confirmed with the help of our vibrational assignments.

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